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           NOVEL SEMICONDUCTOR/CONDUCTING POLYMER INTERFACE
           TECHNOLOGY - SBIR 89.I (A89-083)


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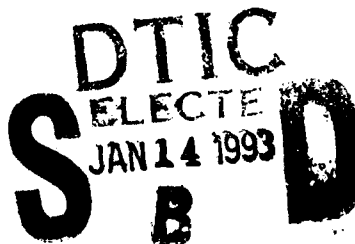

TYPE OF REPORT:   Phase I Final Report


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U.S. DEPARTMENT OF DEFENSE

# SMALL BUSINESS INNOVATION RESEARCH PROGRAM
## PHASE 1 — FY 19 89
## PROJECT SUMMARY

Topic No. A89-083

Military Department/Agency __Army__ .

**Name and Address of Proposing Small Business Firm**

Gumbs Associates, Inc.
11 Harts Lane
E. Brunswick, NJ 08816

**Name and Title of Principal Investigator**

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Signature

P. CHANDRASEKHAR

2/14/90
DATE

**Proposal Title**

"Ultrafast, Broad-band, Passive Laser Shields Based on Novel Semiconductor/Conducting Polymer Interface TEchnology"

**Technical Abstract** (Limit your abstract to 200 words with no classified or proprietary information/data.)

The present work set out to address the critical need for a passive, dynamic (switchable), ultrafast (sub-ns), broad-band (across the Vis.-NIR), durable, yet transmissive ( 75% scotopic transmission in unswitched state) laser shield for protection of personnel eyes against exposure to hazardous laser radiation in combat situations with a novel technology combining inorganic semiconductor (SC) electrodes with novel conducting polymers (CPs) in a single, solid-state interface. The viability of the SC/CP interface switching was eminently demonstrated for a large number of SC-CP combinations, with switching risetimes under pulsed laser radiation at the MPE level in the sub-ns regime for all systems studied, and falltimes in the tens to hundreds of ns. A number of novel, processible (soluble) conducting polymers were synthesized for the first time, and a number of these displayed very broad-band and highly reversible switching behavior. Preliminary CW laser studies showed that a number of interface systems switched in this mode as well. Intrinsic laser-induced polymer switching and nonlinear optical effects in these polymers were also looked at. It was seen that the novel polymers synthesized could be applied commercially as processible conductive coatings for a variety of applications, besides the present application to laser shielding.

**Anticipated Benefits/Potential Commercial Applications of the Research or Development**

An entirely novel ultrafast laser shielding technology will emerge from the completed work, with passive and broad-band application for personnel eyes as well as sensors. In the longer term and commercial sphere, an intrinsic, passive, ultrafast optical switch will emerge which can be used in such fields as optical computing and signalling and optical storage discs. Furthermore, the work has yielded a new class of soluble, processible conducting polymers with applications in IR/Radar signature reduction, EMI shielding, and other fields where processible conductive coatings are required.

**List a maximum of 8 Key Words that describe the Project.**

Ultrafast; dynamic; passive; laser; shield; semiconductor; conducting; polymer.

CONTENTS

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# I. INTRODUCTION

## I.1 TECHNICAL BACKGROUND, NEED FOR LASER SHIELDS, TARGETED LASER SHIELD PROPERTIES

Due to the increasing use of lasers in target identification, range-finding and communcications roles as also potential desctructive use against critical vulnerable targets, including human eyes and sensors [1-6], an imperative need has arisen for protection of military personnel, especially their eyes, from accidental or deliberate exposure to hazardous, potentially debilitating medium-intensity laser radiation in the pulsed and CW regime. The problem has been recently aggravated with the proliferation of both pulsed and CW laser systems and the possible field use of tunable dye-based laser systems.

Laser hazards can be illustrated with a typical example. With the standard 694 nm (ruby) rangefinder laser, if one employs an energy fo 100 mJ/pulse, a 30 ns pulsewidth, 0.25 mrad divergence and 2 cm exit diameter, the beam diameter at 1 km is 25 cm (1 m for a 1.0 mrad divergence), thus greatly increasing the likelihood of contact with personnel eyes, while the energy of the laser at such contact is close to or in excess of the Maximum Permissible Exposure (MPE).

### Targeted Properties for Effective Laser Shields

Essential functional attributes of functional laser filters are ns or sub-ns risetimes, broad-band action (across the visible, near-IR, and in specialized cases, near-UV regions), capability of functioning effectively at laser incident thresholds ranging from tens of $uJ/cm^2$ and higher, and dynamic (switchable), and preferably passive action.

In the just-completed work, targeted properties serving as guides for the work were operation in the 400 - near-IR regions, with a static filter acceptable for the wavelength region in excess of 700 nm, protection under both scotopic and photopic conditions with 1% transmission of hazardous radiation (OD ca. 2.0) in the switched state but at least 75% transmission (OD ca. 0.125) of incident radiation in theunswitched state without alteration of its spectral distribution, and protection against pulses from 1 ns to CW duration. Targeted switching risetimes were in the sub-ns region, with a switched/unswitched OD ratio of ca. 16.0. Additional essential targeted properties were passive operation, inherent in the principle of the technology investigated, and uniformity of shielding for all angels of incidence of laser radiation. Resistance to abrasion and ballistic penetration and functioning under reasonable variables of environmental conditions and temperature were also desirable properties. The switching risetime and falltime targets were substantially achieved or exceeded with all test systems studied.

Table I lists typical lasers in battlefield use from information available to Gumbs at this time, and Table II lists MPE's for eye exposure.

TABLE I: Typical Lasers in Battlefield Use, Including Parameters

| Laser | Wavelength | Energy/pls | P.width | Rate | Pk.power | Use or Plan |
|---|---|---|---|---|---|---|
| Q-Switched Nd:YAG | 1064 nm, 532 nm | 1 J 250 mJ | ~ 10 ns, ~ 10 ns, | 10 Hz 10 Hz | 400 MW 100 MW | target loc./desig |
| Q-Sw. Ruby | 694 nm | 10 J | ~ 25 ns, | 0.5 Hz | 0.2 GW (possible) | tank range- finder |
| Dye (Nd:YAG pmp) | tunable | 50 mJ | ~ 10 ns, | 10 Hz | 10 MW | targ. id., rngfnd, commun. |

Mode-locked Nd:YAG, 1064 nm, 10 mJ, ~30 ps, var.     200 mW  speclz. uses

Ar ion, Excimer, Ga:Al:As, Ti:Al203, Cu vapor lasers all planned to be introduced in near future, according to military information available.

TABLE II: MPE's for a 1 sec. exposure, 3 mm pupil dia., for CW, pulsed lasers, after Stuck et al. [6]. MPEs give total intraocular energy.

| Wavelength | Rate (Hz) | P.width | MPE |
|---|---|---|---|
| 1064 nm | CW | - | 2.5 mJ |
| 1064 nm | 10 | 10 ns | 50.0 uJ |
| 514.5 nm | CW | - | 0.75 mJ |
| 514.5 nm | 10 | 10 us | 0.8 uJ |
| 530 nm | 5 | 15 ns | 5.0 uJ |
| 441.6 nm | CW | - | 0.6 mJ |
| 441.6 nm | 1 | 18 ms | 10.0 uJ |
| 694 nm | 1 | 6 ps | 0.2 uJ |
| 694 nm | 1 | 30 ps | 1.3 uJ |
| 694 nm | 1 | 30 ns | 2.1 uJ |
| 694 nm | 1 | 100 ms | 27.0 uJ |

I.2  BASIS OF PROPOSED TECHNOLOGY -   BRIEF SUMMARY

Conducting polymers are electrochemically switchable reversibly between redox states of varying absorption characteristics across a broad spectral range; typically in the visible region, they possess one redox state that is highly transparent and another that is highly opaque. Fig. 1 shows the contrasting optical density (OD) change across the visible spectral region for electrochemical switching of an exemplary polymer. Extremely broad-band, reversible switching with highly stable polymers is provided.   Conducting polymers (CPs) thus offer the potential for providing effective laser shielding with all attributes as defined above, but electrochemical switching suffers from the drawback of slow rate (typically milliseconds). If an effective means of rapid (e.g. ultrafast, sub-ns) switching of the polymers could be provided, CPs could be used for a viable laser shielding technology.

An efficient and ultrafast method of providing the emf (applied potential) for the CP switching is obtainable by use of an inorganic semiconductor (SC), by direct photoexcitation of the latter, as illustrated in Fig. 2. Furthermore in this case, the SC provides both the emf and the trigger for the CP switching, thus yielding a passive device.

Fig. 3b illustrates the unique application of this technology in an actual device configuration, and compares it with the construction of a simple CP heterojunction device (Fig. 3a). In the latter, the polymer is sandwiched directly between an inorganic SC and an inert metal electrode which are electrically connected. Upon photoexcitation of the SC (e.g. by a laser), the polymer merely provides a conducting medium for electron flow between metal and semiconductor. However, if an intervening medium of low dielectric constant (high resistivity) such as air or inert electrolyte exists in front of the polymer, photoexcitation of the SC leads to forced ultrafast redox (reduction or oxidation of the polymer (Fig. 3b).

Fig. 2 also illustrates the major processes involved in the switching action of the SC/CP interface (illustrated here for an n-type SC and p-type polymer), which can be outlined as:

1) Photoexcitation of semiconductor, occurring in the single picoseconds regime.
2) Charge transfer to polymer, occurring in the sub-nanosecond regime.
3) Oxidation or reduction of initial polymer layers (of ca. 10 - 40 nm thickness), occurring in the sub-nanosecond regime and causing switching of these layers.
4) Charge transport in the bulk polymer, causing the switching of the bulk polymer and occurring in time regimes ranging from nanoseconds to possibly microseconds.

It is thus clear from the above discussion, the switching of the SC/CP interface plainly has the potential for ultrafast operation.

It should also be mentioned that an important criterion in the selection of a suitable SC material is proper matching of its properties not only with the spectral region desired to be shielded but also with the CP to be used in conjunction with it, and this was also investigated widely in the completed Phase I work. The principles of SC-CP matching are discussed more fully below.

## I.3  ALTERNATIVE COMPETITIVE TECHNOLOGIES AND ADVANTAGES OF THE PRESENT TECHNOLOGY OVER THESE

### Alternative Technologies

A wide variety of systems has been used to address the problem of laser shielding, including reflective filters (holographic, dielectric and liquid crystals used in a reflective mode), thermal devices such as $VO_2$ thermistors, combinations of static filters, conducting polymers switched electrochemically, liquid crystals switched electrically, and nonlinear optical (NLO) effect based devices [2]. Of these, the last appear to have shown the most promise and have received the most attention. In this area presently, third order nonlinear susceptibilities in the region of 10**-9 esu or slightly higher have been achieved with further increases making actual device applications practical [7].       The drawbacks of reflective

(primarily optical notch) filters such as holographic or dielectric filters and rugates, include narrow wavelengths of operation and an angle-of-incidence dependence for many of them, and need for pre-filters to concentrate incident radiation in some, making them unwieldy and inflexible for device incorporation.

Other mentioned technologies such as absorbing dyes (e.g. metalloporphyrins), have rapid switching times, but have poor attenuation and stability. Liquid crystals have not been shown to switch in less than several microseconds with available technologies, while thermal based devices such as VO2 thermistors have poor switching rates and non-passive operation. Conducting polymers switched in the conventional, electrochemical way, have slow switching times (sub-ms at most). Thus it appears that a viable technology for effective laser shielding does not yet exist [2,4,8-10].


## Advantages of Proposed Technology Over Alternative Technologies

The proposed semiconductor/conducting polymer (SC/CP) technology possesses major advantages over alternative technologies discussed briefly above, primary among them being the ability to meet the critical requirements for effective laser shields as defined above, including ultrafast, broad-band, passive, stable operation with at least 75% transmission in the unswitched state and 1% or less transmission in the switched state. The advantages specifically are:

a) Dynamic (i.e. switchable) and ultrafast action. Observed risetimes in the sub-ns region and observed falltimes in the ns to ms region.
b) Tailorable broad-band action, through the visible, near-IR and, if required, near UV regions; tailorable by proper selection of conducting polymers used.
c) Passive action. No need for a means of detection of the incident laser pulse and subsequent activation of a laser shield; concomitant to this characteristic:
d) No power requirements.
d) Low cost, estimated at $100's per device.
e) Comparatively low laser protective thresholds, predicted on the basis of the present results to be in the tens of uJ/cm$^2$.
f) Comparatively high laser damage thresholds, due to the innate properties of the polymers used.
g) Ability to protect against ballistic fragments, with suitable encapsulation; radiation hardness.
h) Adaptability to large-area and oddly shaped devices.


## II. OBJECTIVES OF THE PHASE I WORK

The overall technical objective of the work was to prove feasibility of the SC/CP technology for effective laser shielding with a variety of polymers and semiconductors. Specific technical objectives as delineated in the Phase I proposal were:

1) Screen a large number of pre-selected (cf. Table III) polymers for requisite Sw/Unsw OD contrast, electrical properties, spectroelectrochemical properties, stability and reversibility of switching and compatibility with SC materials.

2) Conduct theoretical (quantum mechanical) studies of selected polymers to aid in screening process.

3) Fabricate doped SC electrodes and spectroelectrochemically characterize these. From this and on the basis of 1) above identify optimal SC/CP systems for study.

4) Characterize the switching properties of prototype devices under pulsed laser radiation. Determine both rise and fall times for switching, the Sw/Unsw OD contrasts under pulsed laser conditions.

5) Conduct initial CW laser switching studies for the devices (cf. 4)).

6) Arrive at clear guidelines, on the basis of the Phase I results, for the selection of additional optimal SC/CP systems, and for the construction of actual devices for use with goggles, visors, etc.

For achievement of the objectives, the most important parameters of the switching, such as switching risetime and falltime, reversibility, and degree of protection (or optical density) achieved, were be shown to be applicable to laser eye protection, the final objective of the present work. Targeted switching risetimes were in the single-ns or sub-ns region, targeted falltimes are in the tens to hundreds of ns, and targeted maximum switched optical densities (ODs) were in the range 2.0 to 6.0, with a rest-state scotopic and photopic transmission of at least 50% (rest state OD or 0.303 or less).

Included in the scope of the work was the identification, synthesis, characterization and utilization of new conducting polymer materials with properties superior to those studied earlier and applicable to laser eye protection. Also included was the further testing of these with identified and selected semiconductor materials under laser radiation. Based on these tests, the construction of prototype semiconductor/conducting polymer devices for further testing under both pulsed and CW laser radiation could be undertaken in future work.


## III. WORK CONDUCTED DURING PHASE I


III.1 METHODOLOGY


A more detailed discussion of the methodology appears in the discussin of each aspect of the results in the subsequent sections below. In this section, the methodologies will be briefly summarized for reference.


### Semiconductor deposition

Semiconductor materials, when required as films on glass, were subcontracted to an outside vendor, the Drexler Microelectronics Fabrication Laboratory, Dept. of Elec. Eng., New Jersey Institute of Technology (NJIT), Newark, NJ to be deposited via thermal evaporative deposition. Gumbs has developed a close relationship with Prof. R. Cornely, the Director of the Drexler Laboratory, and was supporting a senior student in his group, Varsha Sheladia, during the course of the Phase I work.

Although initial results obtained at NJIT were good, subsequently, due to the academic work overload of the student and immediate unavailability of replacement students, the work was slowed down during the final phases of the Phase I work. Subsequently, Gumbs re-investigated a number of private vendors who had been initally avoided due to high cost and lack of guarantee for the work, and estabilished contacts which will lead to working relationships with other university semiconductor deposition centers, most notably the Depts. of Physics and Electrical Engineering at Rutgers University, New Brunswick, NJ, very advantageous due to its proximity. When single crystal (CdS, CdSe) materials were required, these were obtained from Cleveland Crystals Inc., Cleveland, OH.

## Theoretical Studies

The semi-empirical CNDO methodology for these has been described at length in the Phase I proposal.

## CW Laser Studies

Preliminary CW laser studies, which served to supplement the more extensive pulsed laser studies, were conducted in-house at Gumbs. These were primarily applicable to CdS and CdSe substrate samples.

For CW studies, an in-house system based on an acousto-optically modulated Ar ion laser, with nominal energy of ca. 20 $W/cm^2$ and multiline emission 458-515 nm and a 200-ps-risetime Si-avalanche photodetector was used.

## Pulsed Laser Studies

All pulsed laser studies, forming the basis of the testing of the switching properties of the SC/CP interface, were conducted at the Regional Laser and Biotechnology Laboratories (RLBL), U. of Pennsylvania, Philadelphia, PA, with which Gumbs has an ongoing relationship. A nanosecond transient absorption instrument, based on a Nd:YAG Q-switched laser operating either in conjunction with a dye laser (when required) or at wavelengths of 532 nm, 355 nm and 1064 nm (fundamental) was used A double-beam analyzing train at 90 degrees to the laser (sample 45 degrees to both) was used, with monitoring delay times from a nominal 0 ns to several milliseconds. The laser normally provided a 5 ns or 8 ns pulse at 10 or 20 Hz, at an energy of 2 - 15 $mJ/cm^2$ (without beam focussing). The probe (analysing) window was 140 nm wide and could be ranged from ca. 350 nm to ca. 800 nm.

Towards the end of the project, some delays were experienced in scheduling of the pulsed laser runs at RLBL due to the departure of its Head of Laser Operations, Dr. Holtom, and lack of immediate replacement, as well as due to overload of other users. The picosecond transient absorption (TA) system which was earlier being set up for Gumbs' use and was scheduled to be ready by the end of 1989 was also delayed for identical reasons, and thus we could not obtain results for characterization of ps-regime risetimes for the successful SC/CP systems.

## Chemical syntheses

For a number of polymers not synthesizable electrochemically, chemical syntheses directly from monomers or through precursor polymers was required.

In addition, the corresponding monomers of a number of polymers which were not available commercially had lengthy and involved syntheses.


## Electrochemical studies

For most electrochemical studies, a computer-controllable Princeton Applied Research Corp. (PARC) Model 273 Potentiostat/Galvanostat, a state-of-the-art electrochemical research instrument, with attached Houston Instruments Model 2200GW X-Y recorder was used.

Electrosynthesizable polymers were polymerized potentiostatically (constant applied potential) directly from monomer solutions either in the 3-electrode or the 2-electrode setup. The polymer was electrodeposited at the appropriate potential on substrates including Au/glass, Pt/glass (ca. 50 -200 A), semiconductor on glass (n-indium tin oxide (ITO), CdS) and semiconductor single crystal (CdS, CdSe, ca. 1 mm thick) from monomer solutions. Large-scale electropolymerizations, especially of soluble polymers, were conducted at pyrolytic graphite electrodes in the 2-electrode mode overnight under nitrogen, using a Micronta dual tracking power supply. The polymers were washed with the solvent of preparation and dried in air prior to characterization.


## Spectroelectrochemical studies

For spectroelectrochemical studies, a special spectroelectrochemical cell with N2 purging and blanketing was used. Spectroelectrochemical (SPEL) characterization curves were generated by potentiostatting the polymer at an appropriate potential and scanning the spectral region of interest with the monochromator; a spectrum of blank substrate in electrolyte served as reference.


## III.2 STUDIES FOR FABRICATION OF AMORPHOUS THIN FILMS OF SEMICONDUCTORS

Gumbs Associates, Inc. had earlier developed a strong relationship with the group of Prof. Roy Cornely, Director of the Drexler Thin Films Microelectronics Laboratory at the New Jersey Institute of Technology (NJIT), Newark, NJ, for semiconductor electrodes fabrication. Prof. Cornely's expertise lies specifically in the field of semiconductor thin films deposition. The NJIT collaboration was decided upon due to initial difficulties had been encountered with Gumbs' attempts to have fabrication of SC electrodes done with commercial vendors. Prof. Sosnowski's group at NJIT under the overall direction of Prof. Cornely was also used for collaboration, and we supported students assigned to Gumbs' work by Prof. Cornely, including Varsha Sheladia, a senior student. Initial fabrication work was done at NJIT very successfully, while delays were experienced later due to the student's intended departure and academic overload and lack of replacement students.

During the first reporting period at NJIT, excellent films, usable as semiconductor electrodes, were fabricated with the following parameters:

  o CdS, Cr-(adhesive) undercoating, undoped, resistivity 10**3 to 10**4 Ohms/square, film quality excellent.
  o CdS, undoped only, resistivity ca. 10**3 Ohms/square, film quality excellent.

o CdS, Cr-adh.u.c., In doped 5 ppm nominal target, resistivity ca. 100 Ohms/square, film quality poor, analysis indicates excess In.
o CdS, In-doped, 50 ppm nominal target, resistivity ca. 50 - 80 Ohms/square.
o CdSe: with and without Cr and Ti adhesive undercoating; undoped and In-doped. Analysis of films obtained thus far have indicated a slight excess of Cd over Se in the 1:1 stoichiometric compound, a new problem not encountered earlier with previous CdSe films. This is currently being investigated.

During the second reporting period, semiconductor thin film deposition studies continued at NJIT, with emphasis on CdSe deposition. Based on an extensive literature search and previous deposition experiments (during the last reporting period) at NJIT, it was found that stoichiometric, 1:1 deposition of CdSe, with which we had had problems during the last reporting period, could be accomplished only with a three-temperature mode of operation, with careful control of CdSe, Se evaporant and substrate temperatures. Accordingly, new equipment was ordered to enable 3-temperature deposition control, and the precise temperature and pressure conditions determined for 1:1 stoichiometric CdSe deposition.

During the third reporting period, work with semiconductor electrodes fabrication continued at NJIT. A large number of additional CdS/glass electrodes both doped (n-doped with In) and undoped, and with an adhesive Cr undercoating, were made. Work continued with the difficult fabrication of CdSe/glass electrodes; nonstoichiometric material continued to be produced, and more exact control of temperature and pressure condictions was being sought with newer equipment on order for the project. CdSe decomposes on thermal evaporation into its components, which redeposit in nonstoichiometric proportions on the substrate. The activity of Se needs to be increased by additional of excess Se to the system, but precise control of stoicniometry requires very accurate pressure and temperature control based on measured calibration curves. Calibration data for this system were collected during this period.

During the fourth reporting period, due to additional student changes at New Jersey Institute of Technology (Prof. Cornely's group), some additional delay was experienced in semiconductor electrodes fabrication. However, excellent additional films of CdS (doped and undoped) were obtained, and the conditions for deposition of useful CdSe films successfully identified. It was hoped that when additional pulsed laser sessions are available at RLBL, these new films could be investigated forthwith in conjunction with the new polymers synthesized during tnis reporting period (see above).

Also during the fourth reporting period, contacts were made with professors in the Dept. of Electrical Engineering and Dept. of Physics/Astronomy at Rutgers University, New Brunswick, NJ, specifically Prof. Robert Bartynski at Physics/Astronomy and Prof. Jian Zhao at E.E., for deposition of thin film semiconductors for our SC/CP interface work. This was to have an alternative to NJIT because of the slow progress there. The persons contacted were favorable to our requests, and financial arrangements were being worked out.

During the fifth and sixth reporting periods, a number of excellent thin film CdS/glass electrodes were obtained from New Jersey Institute of Technology (NJIT). These had purity, conductivity and related properties superior to any obtained so far. It was contended that with superior films of this nature, strong SC/CP interface switching would be observable even for those polymers studied so far that have shown weak switching with CdS, sucn as poly(diphenyl amine) and poly(4-amino-biphenyl).

Also during the sixth period, final arrangements were continued for setting up collaboration with Rutgers University's (New Brunswick, NJ) Electrical Engineering Dept. and with the same department at Princeton U., Princeton, NJ. This was as an alternative to NJIT, at which progress had been slower than accepted in the recent reporting periods. A finalized working relationship with these additional institutions would enable Gumbs to obtain a very wide variety of additional semiconductors for incorporation and testing in SC/CP interfaces.

## III.3 THEORETICAL STUDIES

An important insight into the properties of the polymers synthesized was obtained with theoretical studies based on the CNDO methodology outlined earlier, and this provided a proper handle on the selection of polymers for further study.

During the first reporting period, calculations on poly(isothianaphthene) (PITN) indicated a nominal bandgap of ca. 1.25 eV for the major VB -- CB transition of this polymer, in contrast to the calculations of Bredas et al. quoted in the proposal, which indicated very low or vanishing values of the bandgap of this polymer. This also was confirmed by spectroelectrochemical data on the soluble PITN synthesized by us. Figs. 4 and 5 show spectroelectrochemical data for virgin and reprocessed films of PITN on ITO in tetrafluoroborate/acetonitrile medium. This was a strong test for the greater accuracy and utility of the CNDO methodology adopted here, in contrast to the valence effective Hamiltonian (VEH) and other methodologies adopted by Bredas and others.

Based on theoretical studies during the second reporting period, a prediction was that chemically polymerized copolymers of polythiophenes and polypyrroles with formaldehyde and benzaldehyde would possess broad-band absorptions, high swithed/unswitched OD ratios, and other desirable properties.

During the third reporting period, based on additional literature surveys and some continued theoretical studies, novel polymers with solubility, redox potential location, stability and other parameters most suitable for the present application were identified. Some of these are listed in Table III below.

During the fourth reporting period, theoretical studies, based on CNDO (Complete Neglect of Differential Overlap) methodology incorporating vibrational interactions and configurational interactin (CI) were continued. Based on these, and on additional surveys of the literature, we identified additional very promising monomers whose electropolymerization should yield soluble, processible, highly conductive and low-bandgap conducting polymers especially useful for laser shielding applications. These are listed in Table IV. An important feature of these monomers is that most are readily available commercially. In one case, facile synthesis from a commercially available precursor is required.
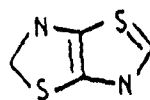
TABLE III: NOVEL, POTENTIALLY HIGHLY SOLUBLE POLYMERS IDENTIFIED, DIRECTLY ELECTROPOLYMERIZABLE, based on the following identified monomers:

thiazole (TAZ) and thiazolothiazole (TTAZ) (below) based polymers;
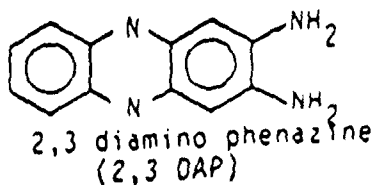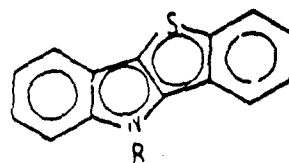dithienobenzene; N-substituted thionapthene indole (both shown below);
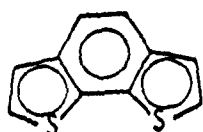
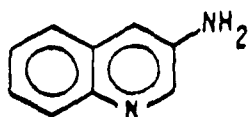dithienobenzene

TAZ

TTAZ

2,3 diamino phenazine
(2,3 DAP)

N-subst. thionapthene indole

TABLE IV:     NOVEL MONOMERS IDENTIFIED, BASED ON THEORETICAL AND
              RELATED STUDIES                                    YIELD-
              ING POTENTIALLY HIGHLY SOLUBLE, WELL-BANDGAP-MATCHED
              (FOR SCs) POLYMERS.


biphenol; phenols substituted with amino groups


p(substituted naphtho [c] thiophenes);      vinylamine based polymers;
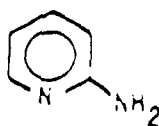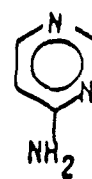


3-amino-                    2-amino-
Quinoline                   Pyridine                2-(left) and 4-(right)-
                                                    amino pyrimidine
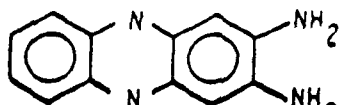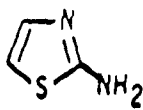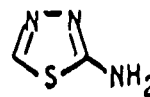



2,3 diamino phenazine  2-amino       1,3,4-Thiadi-    2-amino-1,3,4-
(2,3 DAP)              Thiazole      azole            Thiadiazole

## III.4 NOVEL SOLUBLE, PROCESSIBLE CONDUCTING POLYMER SYNTHESES

### First reporting period

Table V below lists in summarial form additional and in many cases entirely novel conducting polymers synthesized during this period. Additional polymers showing much promise were poly(aromatic amines), additional substituted poly(thiophenes), additional substituted poly(carbazoyls) and several chemically polymerized copolymers, including additional ones based on benzaldehyde and formaldehyde as co-monomer materials.

---

TABLE V: NEW POLYMER SYSTEMS SYNTHESIZED AND CHARACTERIZED. (N.B.: p= poly; Sw/Unsw ODrR= max. switched/unswitched optical density ratio; (C)= chemically polymerized, electrochemically doped; (E)= electrochemically polymerized and doped; abs= absorption; cyclability denotes number of electrochemical cycles between oxidized and reduced states for less than 5% degradation in cumulative properties).

### A. Counterions used:

tetrafluoroborate (most frequent counterion); hexafluorophosphate; p-toluene-sulfonate; perchorate; chloride;

### B. Polymers investigated:

| Polymer | Conductivity (S cm⁻¹) (with (BF4)-) | Spectral Char. & Sw/Unsw ODR | Cyclability |
|---------|--------------------------------------|------------------------------|-------------|
| p(N-Me-pyrrole)(E) | $10^{**-4}$ | sharp abs. regions, poor (3.0 - 6.0) | 350 |
| p(isothianaphthene)(E) | $10^{**-3}$ | some broad-band in NIR, 3.0 - 9.0 | 700 |
| p(dodecyl thiophene) (E) | $10^{**-4}$ | crossover (isosb.) point mid-visible, 3.0 - 9.0 | 650 |

POLY(AROMATIC AMINE) ANALOGUE POLYMERS (all (E)):

---

An additional, highly significant result obtained was the synthesis of highly soluble, and hence highly processible conducting polymers. For instance, the poly(aromatic amines) had typical solubilities in DMF of ca. 5% to 8% w/w.

This is extremely useful for fabrication of semconductor/conducting polymer interfaces, as the conducting polymer then merely needs to be deposited on the semiconductor from solution, and odd-shaped or hard-to-reach device configurations also present no problem.

## Second reporting period

During this reporting period work was continued with the development of new polymer materials with potentially superior solubility (processibility), switching and other properties for application to laser shielding. The additional polymers listed in Table VI were investigated. Of particular importance were the properties of the additional poly(aromatic amines), especially solubility. Most of these polymers dissolve in DMF (N,N'-dimethyl formamide), without leaving any residue (which usually results from insoluble, higher molecular weight polymer chains). Thus poly(4-amino-biphenyl), (PABP), for instance has a w/w% solubility of ca. 6% in DMF, and poly(diphenyl amine), (PDPA) has a solubility in DMF of greater than 10%. The polymers listed in Table VI were for the most part those identified for study in the Phase I proposal.

Much success was obtained in reprocessing many of the above polymers (i.e. recasting films from DMF solution), particularly p(amino-biphenyl) (PABP), p(diphenyl amine) (PDPA) and p(N,N'diphenyl benzidine) (PNNPhe2Bz). Reprocessing will aid considerably in the ultimate fabrication of actual laser shielding devices.

---

TABLE VI: Novel polymers synthesized and characterized. (N.B.: p= poly).

A. <u>Counterions used</u>: tetrafluoroborate.

B. <u>Polymers investigated</u>:

| Polymer | Conductivity (S/cm) | Solubility/DMF | Cyclability |
|---|---|---|---|
| p(benzidine) (PBZ) | 10**(-4 to -5) | 1.5 % w/w | good |
| p(p-phenylene-vinylene) (PPV) | 10**(-3) | precursor ca. 25% | poor |
| p(4-amino-biphenyl) | 10**(-1) | 6.5% | good |
| p(diphenyl amine) | 10**(-1) to 10.0 | grt. thn. 10% | good |
| p(N,N'diPhe-benzidine (reference, synth. earlier) | 10**-4 to 1.0 | ca. 1.0% | good |

---

## Third reporting period

Studies on the following additional promising conducting polymers, identified based on earlier theoretical and experimental work with poly(aromatic amines), were initiated during the present reporting period.

o poly(1,4 phenylene diamine); poly(1,2 phenylene diamine);
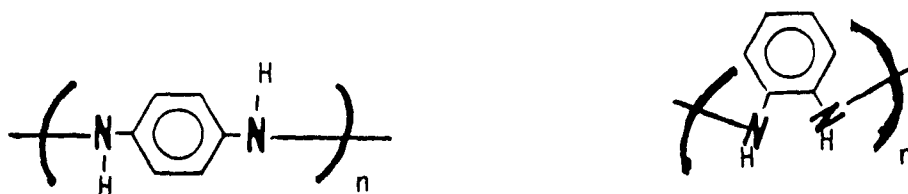


o poly(1,3 phenylene diamine);   poly(3,3',5,5' tetramethyl benzidine).



Preliminary studies with the monomers of the above polymers indicated that electropolymerization was facile and that the benzidine based polymer displayed some significant solubility in organic media like its analogs studied earlier. These polymers' redox potentials were extremely well matched to the most studied semiconductor electrode materials in this project, viz. CdS/glass and CdSe/glass, and their solubilities further increased their advantages for processing into practical SC/CP devices.

Reprocessing studies with other poly(aromatic amine) polymers and with poly(isothianaphthene) (PITN) showed that polymers reprocessed (recast) from DMF solutions were spectrally and electrochemically active, and had properties equal or superior to virgin polymers. Figs. 6a-b, and 7a-b show characterization cyclic voltammgrams for virgin and reprocessed films for selected polymers, while Figs. 8a-c show characterization cyclic voltammograms for other soluble polymer synthesized earlier.

### Fourth reporting period

During this period, a number of additional monomers were identified, based on the theoretical studies, for electrosynthesis. Of these, only 1,4 phenylene diamine, 1,2 phenylene diamine, 1,3 phenylene diamine and 3,3'5,5' tetramethyl benzidine, identified in the previously, were tested for electropolymerization. The last of these in particular yielded highly ordered, highly soluble polymer, with bandgap data matching bands for CdSe and other semiconductors in SC/CP interfaces. The other three monomers yielded oligomers of various chain lengths but no definitive polymer films. Characterization studies were continued for 3,3'5,5' tetramethyl benzidine.

## Fifth, sixth reporting periods

Earlier, a number of new monomers were identified for polymerization studies, primarily amino naphthalenes or thiazoles. During the fifth and sixth periods, additional monomers as identified in Table VII were studied. These displayed potentially very high conductivity, because of the planarity and extensive Pi-delocalization of their structures, and high stability as well. Electrochemical characterization indicated highly reversible behavior and cyclability for the polymers as well.

TABLE VII: ADDITIONAL MONOMERS STUDIED FOR ELECTROPOLYMERIZATION.
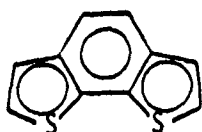


dithienobenzene
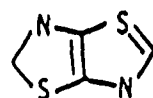
(Thiazole) TAZ

(Thiazolothiazole) TTAZ
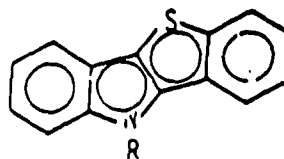
N-subst. thionapthene indole

## III.5 PULSED LASER STUDIES

One of the major findings of the pulsed laser studies was a confirmation of the SC/CP interface switching, with characterized risetimes identically in the sub-ns regime and falltimes in the tens of ns. Thus the pulsed laser studies provided strong confirmation of the eminent feasibility of the proposed technology.

The pulsed laser studies were conducted entirely at the Regional Laser & Biotechnology Laboratories (RLBL) of the U. of PA, Philadelphia, PA, with which Gumbs now has a close working relationship. During Phase I, only the ns-regime transient absorption (TA) instrumentation was utilized; we had been informed earlier that a ps-regime TA instrument was being completed for Gumbs' use, but due to personnel changes at RLBL, this did not materialize.

During the Phase I work, a basic pump-and-probe methodology in the ns time regime was used; a schematic of the apparatus has been given in the Phase I proposal. SC/CP test interfaces were photoexcited (pumped) with ca. 8 ns pulses of energies in the range 80 uJ/cm$^2$ to 10 J/cm$^2$ at 355 nm, 532 nm or variable wavelength (when a dye laser was used) and the decay of the transient absorption of the interface monitored in the region 380 - 800 nm at delay times of nominal 0 ns to 50 ms. An analyzing beam at 90 degrees to the laser (with the sample set at 45 degrees to both, see figure) is used in a double-beam experiment averaging 200 shots at 10 - 20 Hz, thus ensuring that the data obtained reflected highly reversible behavior; a diode-array detector interfaced to the Nd:YAG laser Q-switch via a time-delay generator was used. The entire laser apparatus was controlled by a personal computer. The two Xe flash lamp analyzing beams were ca. 1.5 cm apart. The final TA spectra reflected a calculation based on three measurements each of 200 shots: a dark counts measurement, a reference measurement with no laser, and a signal measurement with the laser illuminating the lower beam spot, thus compensating for any sample inhomogeneity. The possibility of 'crosstalk', i.e. the possibility of laser excitation being transmitted to the non-laser illuminated spot along the semiconductor was seen to be non-existent via control experiments where the SC/CP interface was scribed between the two spots to eliminate any electrical connection.

### First reporting period

Figs. 9A-B and 10A-B show pulsed laser induced TA spectra for SC/CP systems as identified, The polymer films are in these cases rather thick, ca. 300 - 600 nm, and thus in effect what one is seeing is the relatively small OD change of the laser activated beam spot over the unactivated spot from switching of the intial, surface layers of the conducting polymer. Finally, Figs. 11A-B and 12A-B show, for illustrative purposes only, TA spectra for direct laser photoactivation of the polymers, primarily as solutions, at 532 nm. The broad-band responses are especially noteworthy.

All of the above SC/CP systems studied via laser TA spectra showed switching risetimes in the sub-ns region and falltimes ranging from ca. 10 ns to ca. 200 ns.

### Second reporting period

Figs. 13 A-D show transient absorption spectra for the poly(N,N'-diphenyl benzidine)/indium-tin-oxide (PNNPhe2Bz/ITO) interface for a 355 nm pump wavelength. Although this pump frequency is just short of the visible spectral region, it is used for demonstration of feasibility studies only, primarily because it is extremely easy to generate and because it is needed to photoexcite ITO, which is again an easy-to-work-with, commercially available material. These studies were subsequently extended to the mid-visible spectral region, at 532 nm, or to 694 nm.

## Third, fourth reporting periods

Because of personnel changes at RLBL (Dr. Gary Holtom, Head of Laser Operations, left for Battelle Northwest Labs. (Washington State)), delays in scheduling were experienced. As a consequence, no new pulsed laser sessions at RLBL were available during these periods. Dr. C. Mark Phillips was scheduled to take charge as the new Head of Laser Operations. Subsequently, preliminary studies were undertaken of the many novel, highly processible polymers that were synthesized during the last two reporting periods, coupled with new films of CdSe and other semiconductors also obtained during these periods, to demonstrate that the SC/CP switching is a generic phenomenon applicable to all SC/CP interfaces.

## Fifth, sixth reporting periods

During these reporting periods, experimental setups were identified and completed for extensive studies of NLO effects in these novel conducting polymers. Nonlinear Transmission (NLT), Third Harmonic Generation (THG), and Degenerate Four Wave Mixing (DFWM) are three efficient methodologies for this characterization. The setups are described subsequently.

## III.6 CW LASER STUDIES

Preliminary CW laser studies, which served to supplement the more extensive pulsed laser studies, were conducted in-house at Gumbs. These were primarily applicable to CdS and CdSe substrate samples.

For CW studies, a Newport Model C-2001-65ML Ar ion laser, with nominal energy of ca. 20 W/cm$^2$ and multiline emission 458-515 nm was placed at 90 degrees to an optical train for single wavelength monitoring comprising an Oriel Model 6657 Xe source, 77250 monochromator, and associated optics, and a Newport Model 877 APD 200-psec-risetime Si avalanche photodetector connected to a Tektronix Model 2210 or 7514 Digital Storage Oscillosopes. The laser beam was expanded to a 1 cm diameter with optics, and the laser and analysing beams intersected at 90 degrees at the sample which was at 45 degrees to both. The laser beam was modulated before expansion with an Isomet Model 1205-C acousto-optic modulator driven by an Isomet Model 222A-1 driver in turn powered by a pulse generator providing pulses of from seconds in duration to 0.1 millisecond, the smallest available. With the smallest, 0.1 ms pulsewidth, the effective laser energy per pulse was 8.2 uJ/cm$^2$ at the sample, whilst with a 1 ms pulsewidth it was 82 uJ/cm$^2$.

Fig. 14(A-C) show exemplary CW laser data for the CdSe/poly(N,N'diphenyl benzidine) SC/CP system. It can be seen that the risetimes and the falltimes are several orders of magnitude slower than the corresponding times for the same system under pulsed laser activation (data reported earlier). This may be attributed to the lower net energies of the CW laser system: in order to accumulate sufficient charge for transfer to the conducting polymer for sufficient switching of the latter to cause an observable OD change, the semiconductor needs to be exposed to the lower energy CW laser for a longer period of time.

## III.7 NONLINEAR OPTICAL (NLO) EFFECTS IN NOVEL SOLUBLE CONDUCTING POLYMERS IN CONJUNCTION WITH SC/CP INTERFACE SWITCHING FOR ENHANCED LASER SHIELDING

A unique advance during this reporting period was the use, based on

theoretical predictions of third order nonlinear optical (NLO) effects in the novel, highly soluble and conductive conducting polymers synthesized during the course of this Phase I work, of NLO effects in these novel polymers as an assist in to further enhance the laser shielding capability of the polymers in the SC/CP interfaces. Thus with this advancement, a second ultrafast, passive process could be used in addition to the normal SC-induced photo-oxidative switching of the polymers to contribute to the overall laser shielding effect.

NLO effects in conducting polymers have been widely studied in industrial and government laboratories as effective materials for ultrafast (sub-ps), passive laser shields. It has been widely established in particular that high conductivity, high order, and high solubility (also indicating greater order) and low bandgap are very closely related to large NLO effects in these materials. For instance, values for Chi(3), the bulk second hyperpolarizability, of ca. 10**-8 esu have been observed in conducting polymers with high conductivity, solubility and low bandgap, such as those recently studied by Jenekhe. Thus the polymers synthesized during the present Phase I work, which, as has been described at length above, have exceptionally high solubility (8 w/w% in organic media) and conductivity (1,000 S/cm), provide ideal materials for highly enhanced NLO effects. This was borne out in the present period with theoretical calculations.

## Theoretical Studies for NLO Applications

Theoretical studies were initiated with Prof. K. Krogh-Jespersen at Rutgers University. In particular, the work involved calculation of first and second bulk hyperpolarizabilities for poly(aromatic amines) and related polymers which are highly soluble and conductive, from first principles.

The bulk hyperpolaizabilities of a polymer matrix are just an average of the microscpoic hyperpolarizabilities taking into account the number, N, of active contributing molecules, the rotation matrix, $R_{(\theta,\phi,\psi)}$ , which transforms the bulk frame of reference into the molecular principal axes, and the Lorentz local field correction factors, f. Thus, for instance, for the third order nonlinear susceptibility, Chi(3), an expression similar to:

$$\chi_{ijk}^{(3)} = N (R_{iin} R_{jn} R_{kp} f_{mq}^{\sim} T_{qrs}(-\omega:\omega_1.\omega_2) f_{nr}^{\sim} f_{ps}^{\sim})$$

$$. \ . \ . \ . \ .(1)$$

can be used (with standard notations for the axes). A semi-empirical approach exactly identical to that for theoretical calculations described earlier was used for NLO properties computations as well. For each polymer, a detailed electronic energy levels and band structure calculation is conductedm based on CNDO/CI methodology. These computed electronic energy levels and their populations are then used to arrive at the microscopic hyperpolarizabilities (e.g. beta and gamma), which when treated in the manner described in Eq. 1 above yield the corresponding bulk susceptibilities (Chi(2), Chi(3)).

Based on the theoretical predictions, it appeared that the poly(aromatic amines), especially those based on the poly(diphenyl amine) skeleton, would have the largest third order NLO effects, e.g. upto ca. 10**-8 esu for Chi(3), although this would have to be demonstrated experimentally. In the calculations, for each polymer skeleton studied, a number of variables are

considered, for instance the substituent groups at alpha- and beta- positions on biphenyl rings, type of dopant used, polymer chain length and length of bipolaron units considered (in terms of monomer units).

### Experimental NLO Effect Measurements

Experimental setups were identified and completed for extensive studies of NLO effects in these novel conducting polymers. Nonlinear Transmission (NLT), Third Harmonic Generation (THG), and Degenerate Four Wave Mixing (DFWM) are three efficient methodologies for this characterization. Apparatus for characterizations based on these techniques have been arrived at by Gumbs personnel at RLBL; these are depicted in Figs. 15 (NLT), 16 (THG) and 17 (DFWM) respectively. Towards the end of the Phase I work, priority was given to these studies at RLBL over the SC/CP interface switching studies.

## IV. PLANNED, ACHIEVED SCHEDULING OUTLINES FOR TASKS

The scheduling is indicated below. Actual progress is indicated by the solid line and scheduled work by the broken line.

| TASK / MONTH | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| 1. CP Screening | - - - - - - | | | | | |
| 2. Theoretical Studies | - - - - - - - - | | | | | |
| 3. Pulsed Laser Studies | | | | - - - - - - | | |
| 4. CW Laser Studies | | | | | - - - - - | |
| 5. Final Report | | | | | | - - - |

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## VI. FIGURES

(Overleaf et seq.)

FIGURE 1

poly(3-R-thiophene), R= long-chain alkyl, on ITO

FIGURE 2

**Rest state**

Solid or Liquid Electrolyte

Polymer
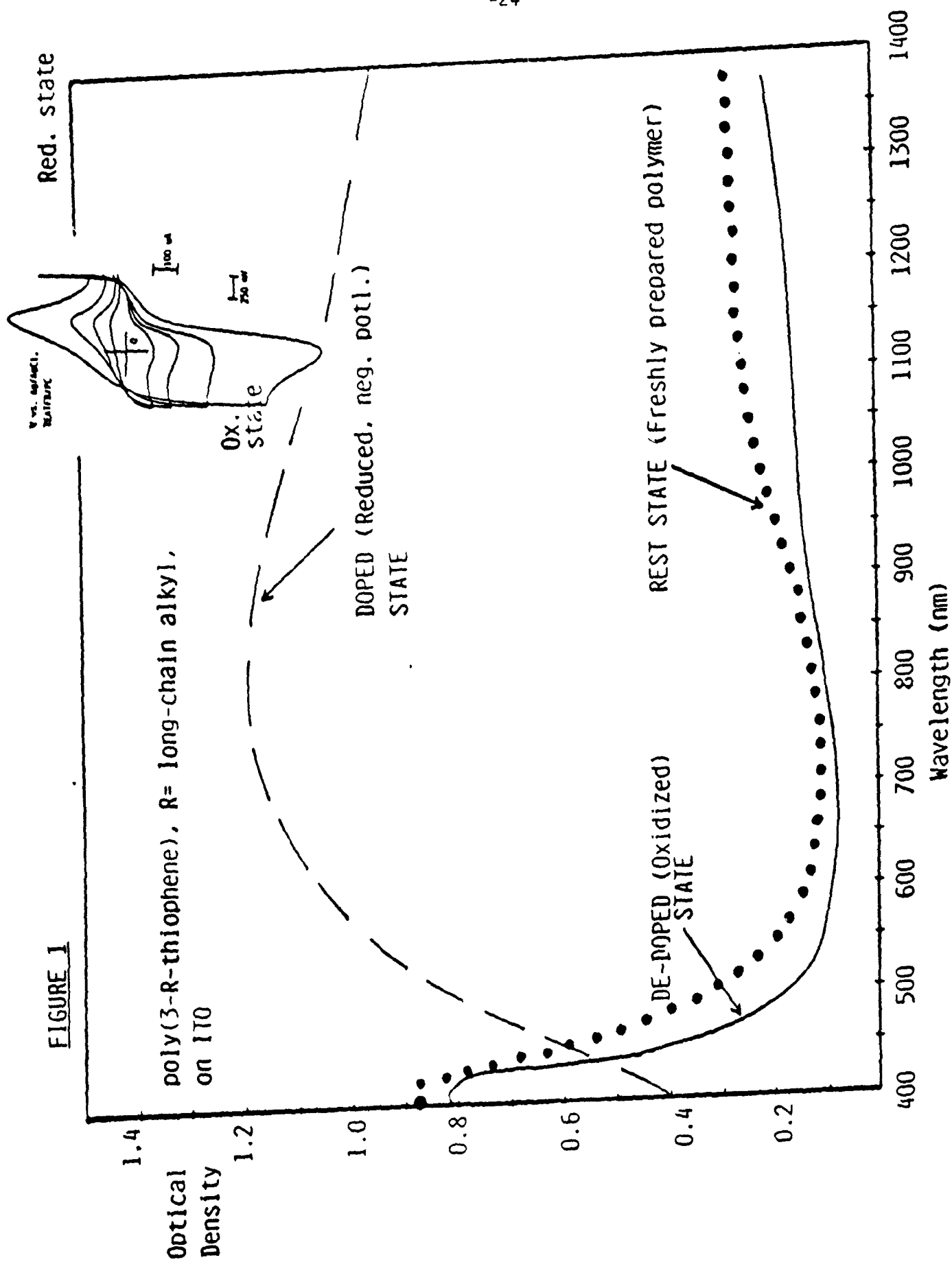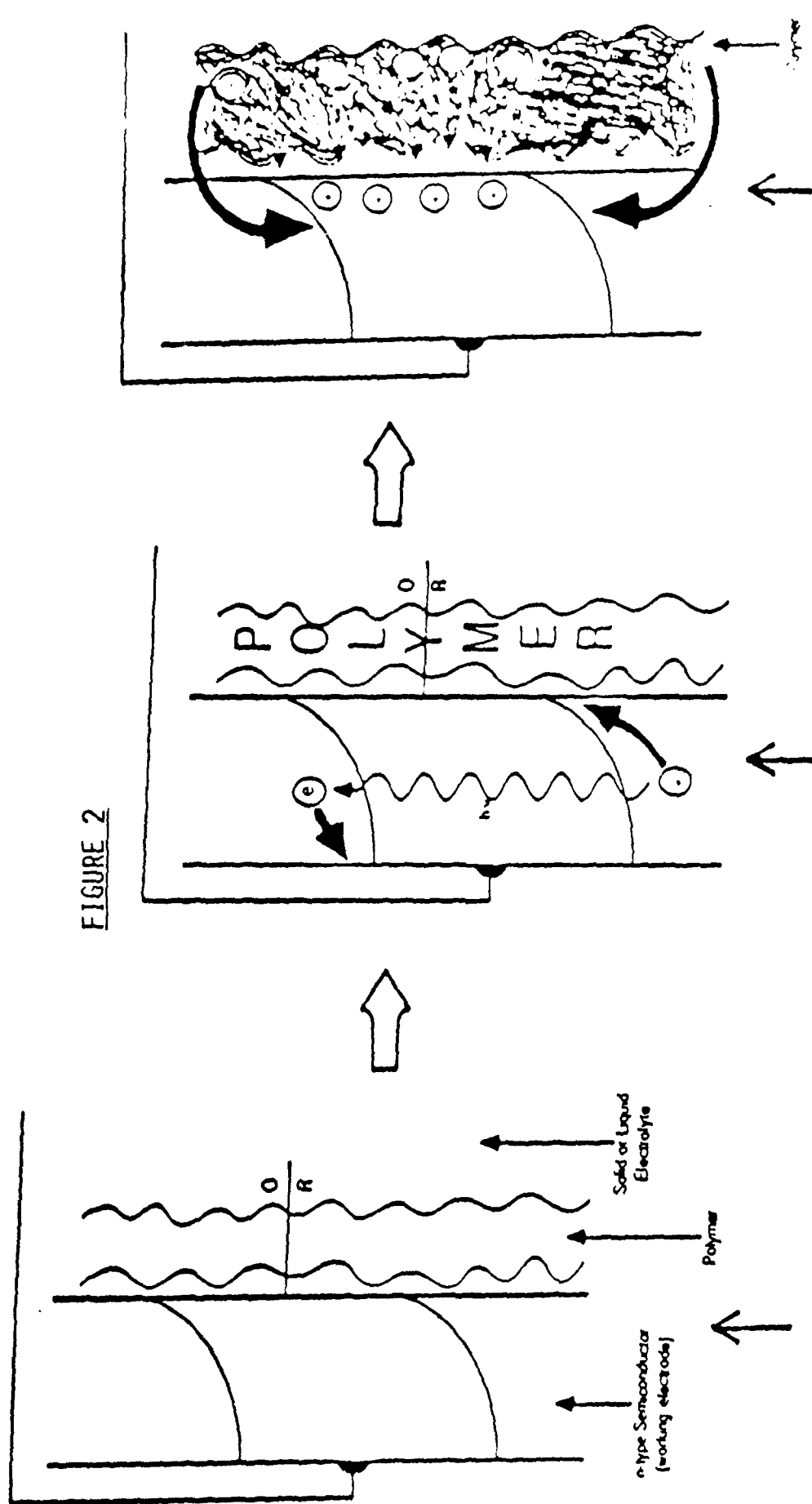
n-type Semiconductor (working electrode)

**Laser excitation**

P O L Y M E R

O R

**Charge transport in polymer:** polymer switching

Processes:

1) Photoexcitation of semiconductor (single psec)
2) Charge transfer to polymer (sub-nsec)
3) Oxidation (reduction) of initial polmer layers (ca. 10 - 40 nm) (sub-nsec), thus switching of these layers
4) Charge transport in bulk polymer, switching of bulk polymer (nsec?)

# FIGURE 3

## Difference between heterojunction device and SC/CP interface

**Heterojunction device**



**SC/CP interface**



(a)

(b)
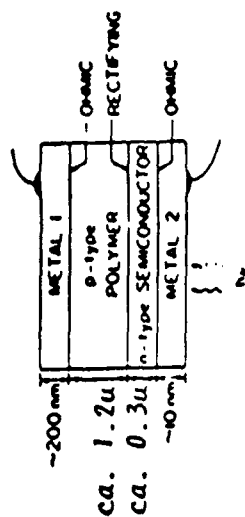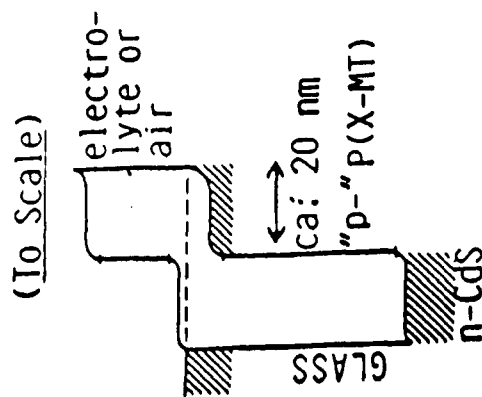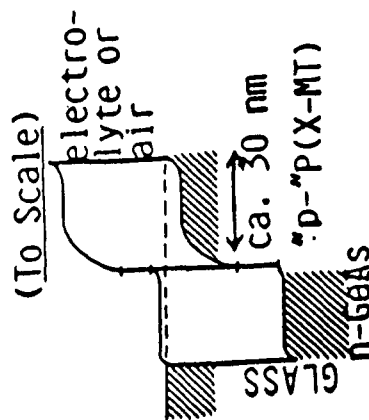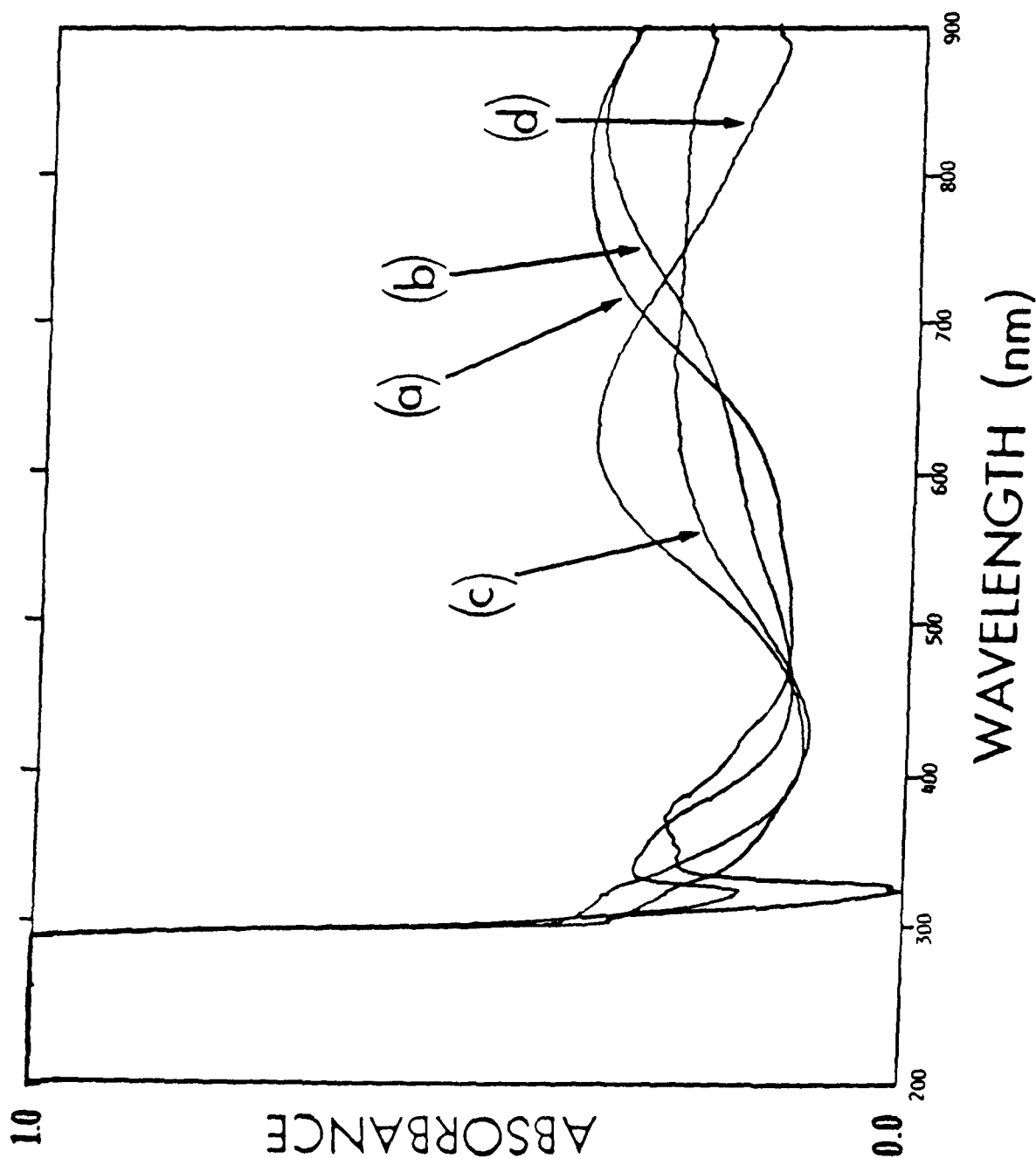
FIGURE 4:
Spectroelectrochemical
characterization curves
for PITN/ITO, virgin
(freshly prepared)
films, in $Et_4NBF_4/CH_3CN$;
a) +1.0 V, b) +0.675 V,
c) +0.18 V (open circuit),
d) -0.5 V.
All vs. Ag/AgCl.



ABSORBANCE

WAVELENGTH (nm)

FIGURE 5:
Spectroelectrochemical
characterization curves for
reprocesssed PITN/ITO (i.e.
films recast from DMF soln.),
in Et$_4$NBF$_4$/CH$_3$CN. a) +1.0 V,
b) +0.675 V, c) open circuit,
(+0.208 V), d) -0.5 V, all vs.
Ag/AgCl.
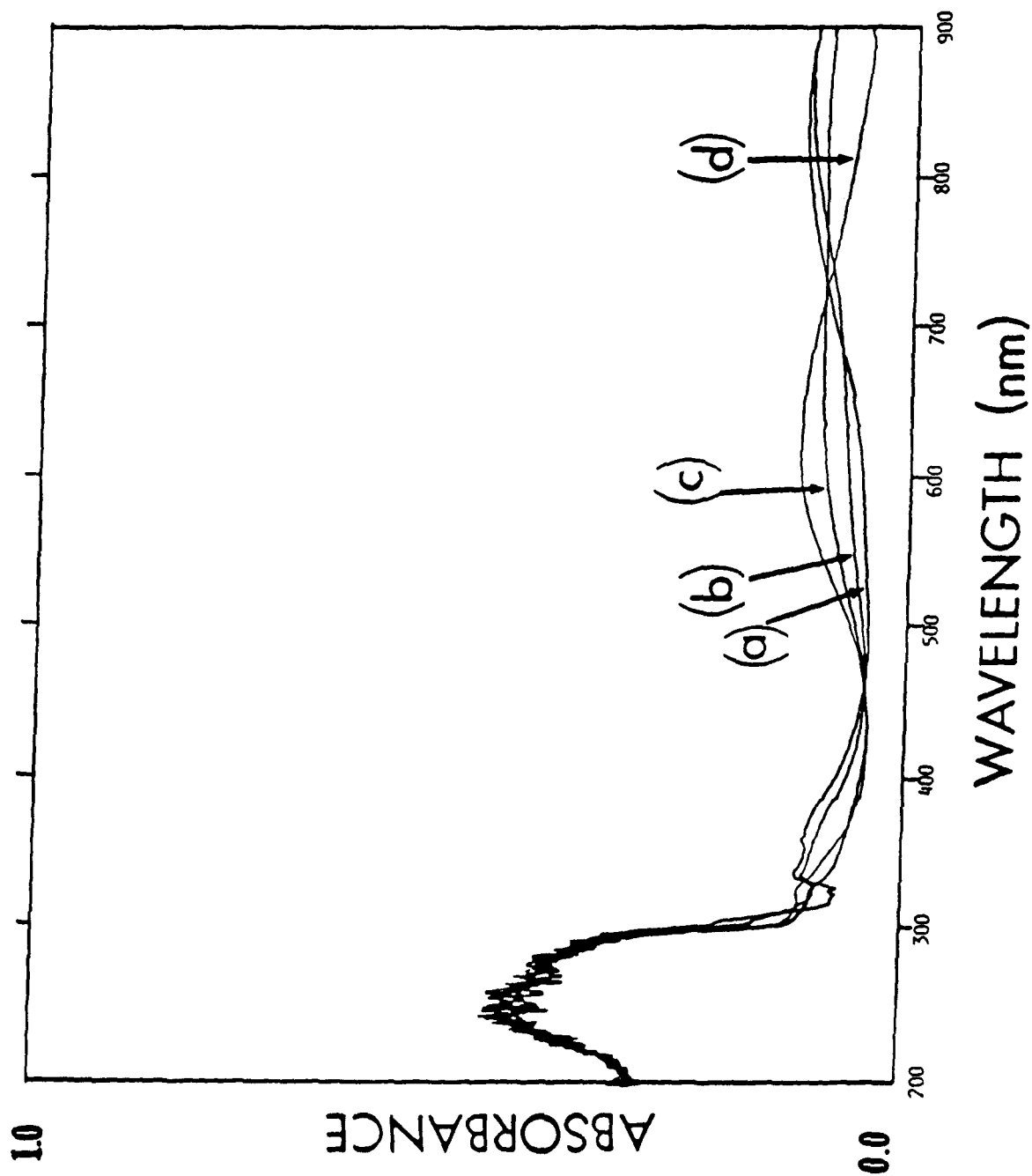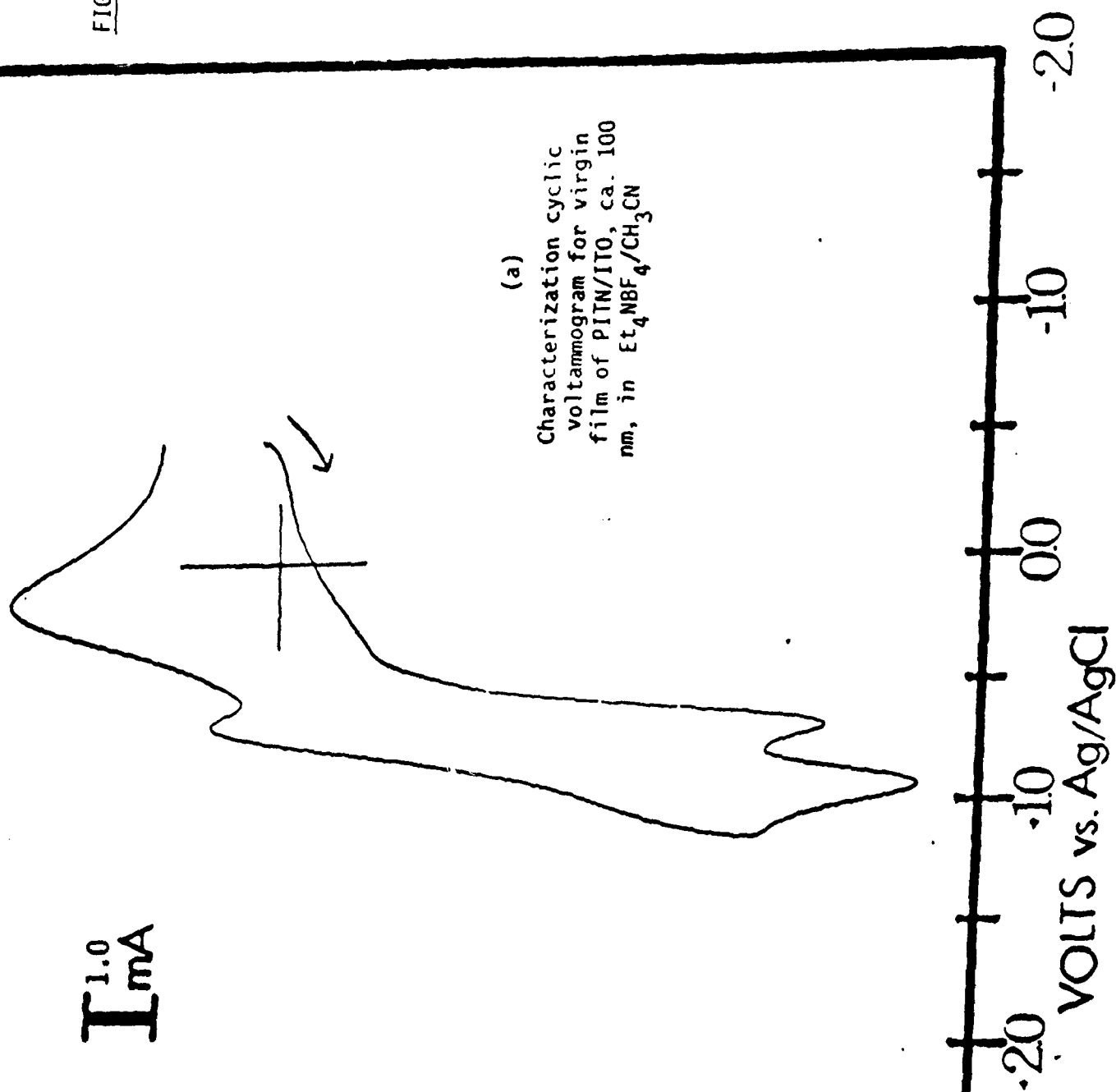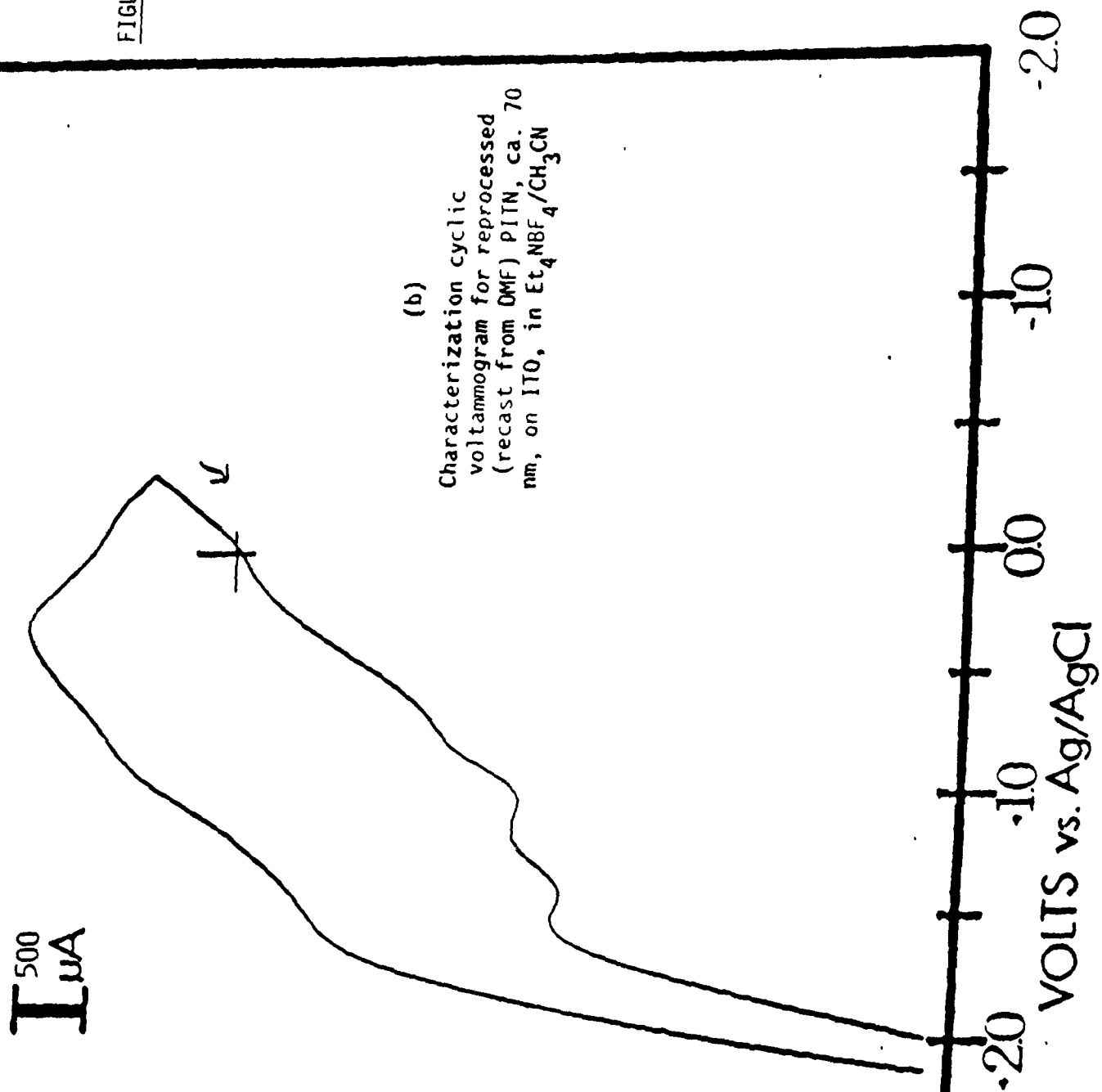


WAVELENGTH (nm)

ABSORBANCE

FIGURE 6a

(a)

Characterization cyclic
voltammogram for virgin
film of PITN/ITO, ca. 100
nm, in $Et_4NBF_4/CH_3CN$

VOLTS vs. Ag/AgCl

FIGURE 6b

(b)

Characterization cyclic voltammogram for reprocessed (recast from DMF) PITN, ca. 70 nm, on ITO, in $Et_4NBF_4/CH_3CN$

VOLTS vs. Ag/AgCl

polyin.N'-di-Phe-benzidine). ca. 1.2 v. on ITO.
in 0.1 M TBAP/ACN. 100 mv/sec



(a)

500 uA

0  -1.0 V

Volts vs. Pt

250 mv
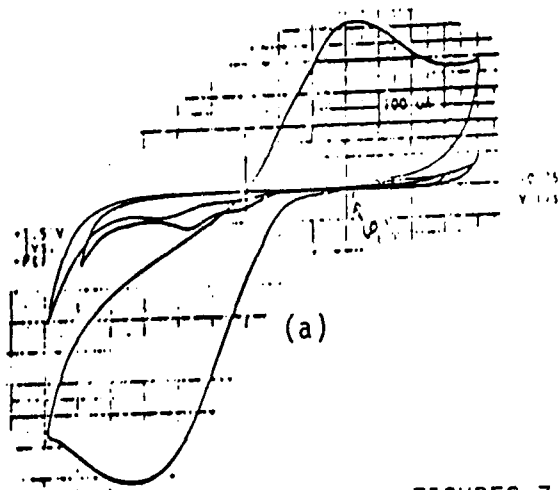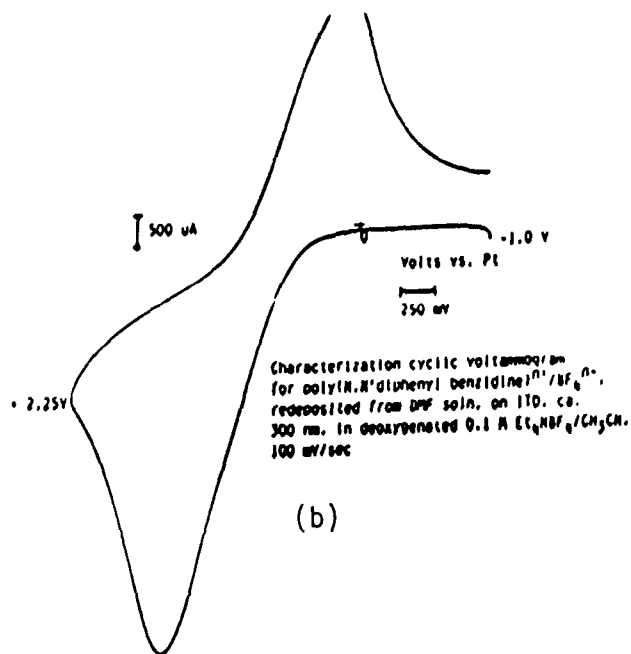
Characterization cyclic voltammogram
for poly(N.N'diphenyl benzidine)$^{n+}$/BF$_4$$^{n-}$.
redeposited from DMF soln. on ITO. ca.
300 ms. in deoxygenated 0.1 M Et$_4$NBF$_4$/CH$_3$CN.
100 mv/sec

(b)

2.25V

FIGURES 7a-b

Characterization cyclic voltammogram for
poly(4-amino biphenyl)$^{n+}$/BF$_4$$^{n-}$. ca. 200 ms.
deposited from DMF soln. on ITO. in deoxyg.
0.1 M Et$_4$NBF$_4$/H$_2$O. 100 mv/sec. indicating
oxidative dissolution (decomposition) in this
medium

(a)

750 uA    250 mv

0  Volts vs. Pt

+1.5 V    -1.0 V

500 uA    -1.0 V

0  Volts vs. Pt

250 mv

Characterization cyclic
voltammogram for poly(di-
phenyl amine)$^{n+}$/BF$_4$$^{n-}$. on ITO.
deoxygenated 0.1 M Et$_4$NBF$_4$/
CH$_3$CN. 100 mv/sec.. just prior
to dissolution.

(b)

-0.875V

FIGURES 8a-c

(c)

50 uA

-0.75 V

0  Volts vs. Pt

250 mv

Characterization cyclic volta-
mmogram for poly(pen)/di(ne)/ITO.
ca. 50 ms. in 0.1 M (Et$_4$N)$^+$/CH$_2$Cl$_2$.
dopant BF$_4$$^-$. scan rate 100 mv/sec?

-0.75 V
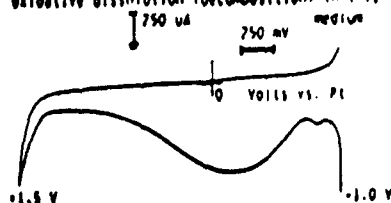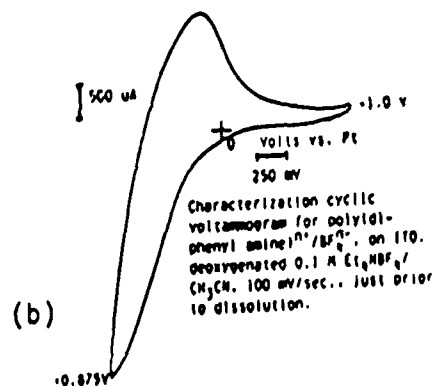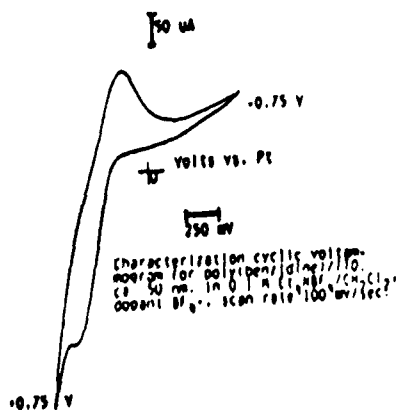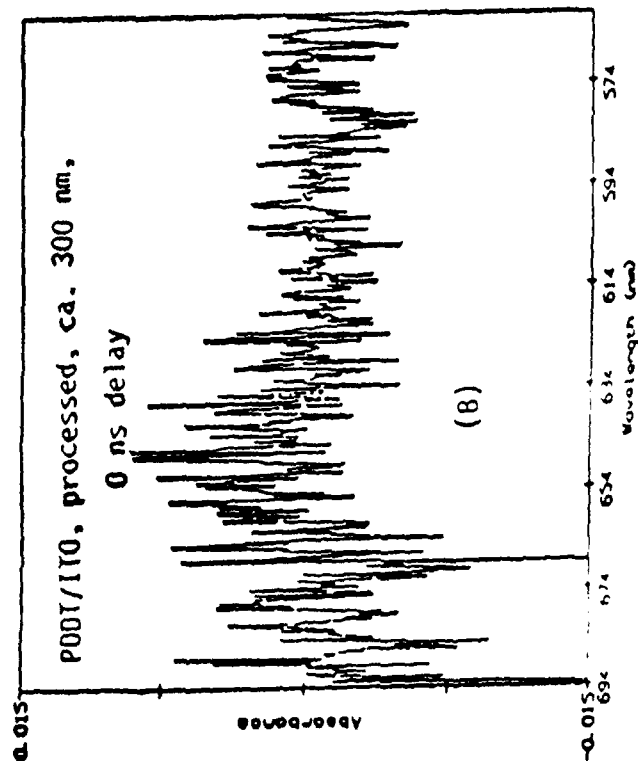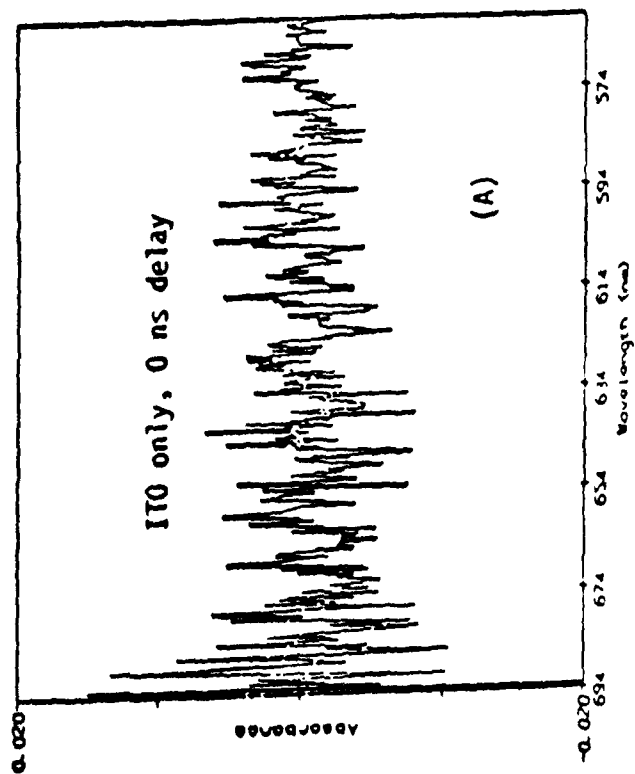
PUMP: 355 nm, ca. 5 ns, ca. 2 mJ/cm$^2$, 100 shots, unfocussed beam.
(N.B.: PDDT = poly(3-dodecyl thiophene); the film is prepared from a saturated chloroform solution)

FIGURES 9A-B
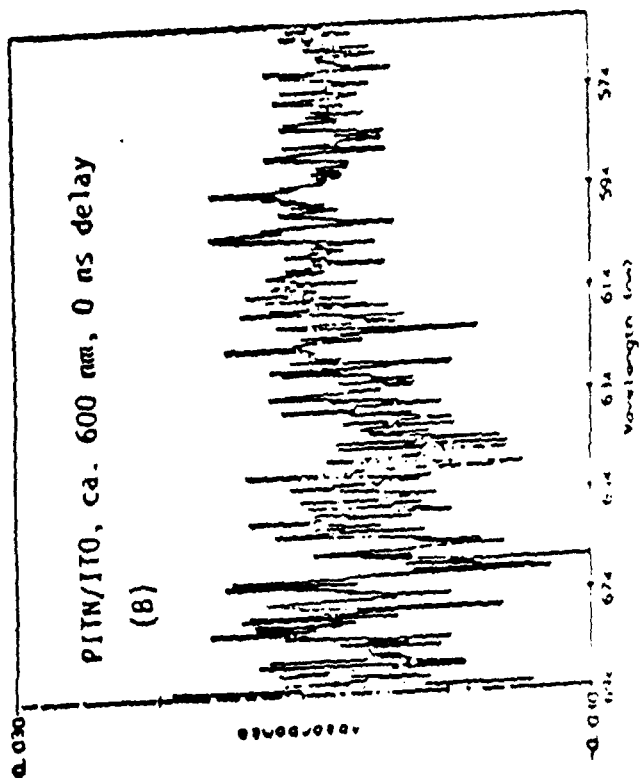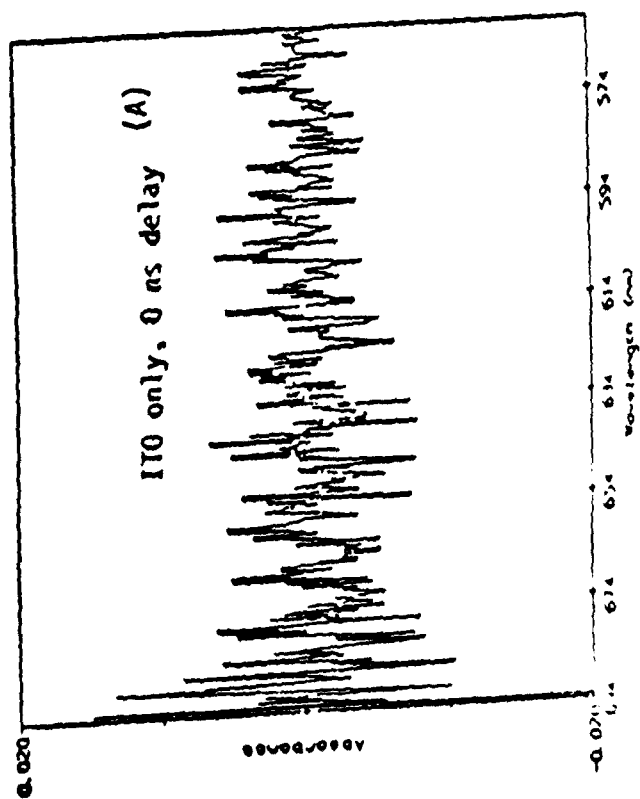
PUMP: 355 nm, ca. 5 ns, ca. 2 mJ/cm$^2$, 100 shots averaged, unfocussed beam. N.B.: PITN = poly(isothianaphthene)
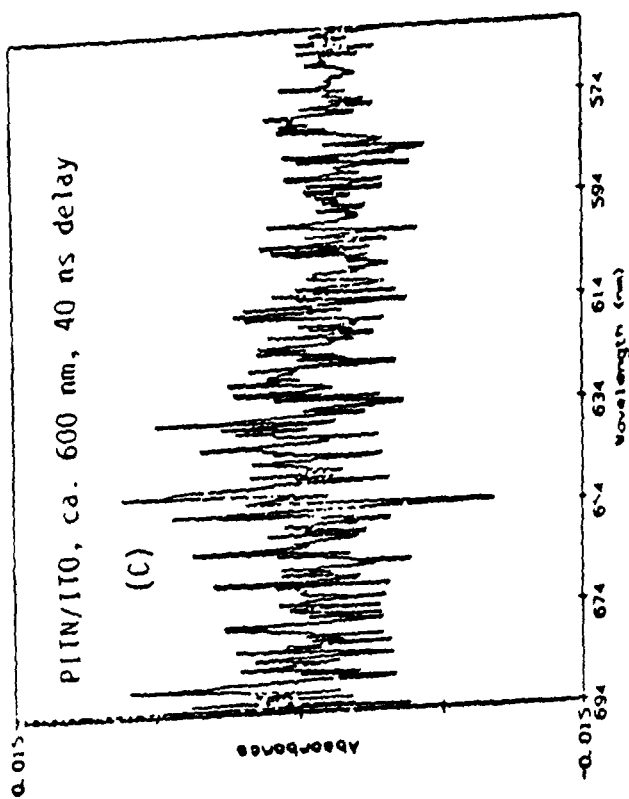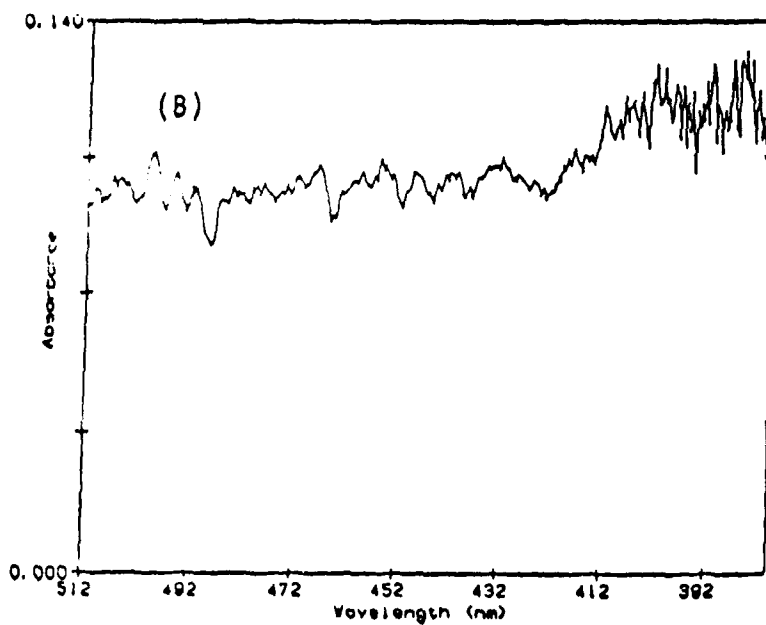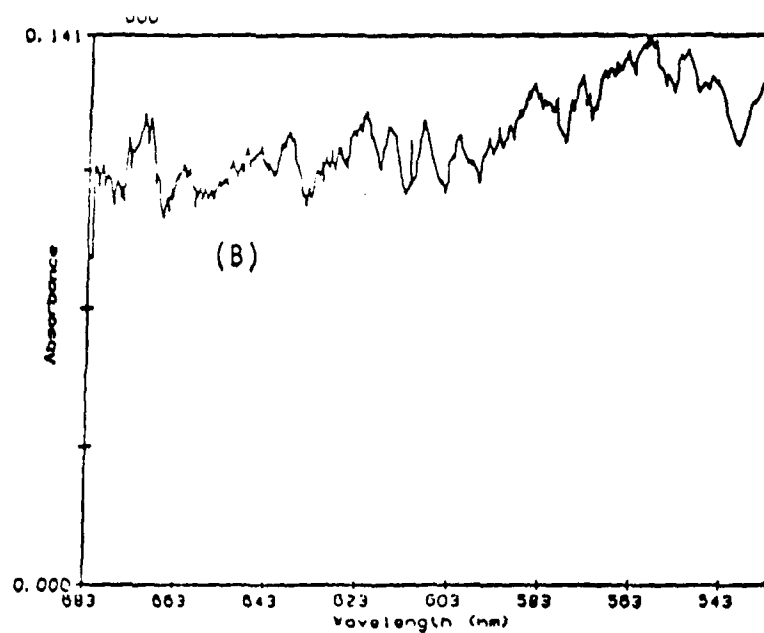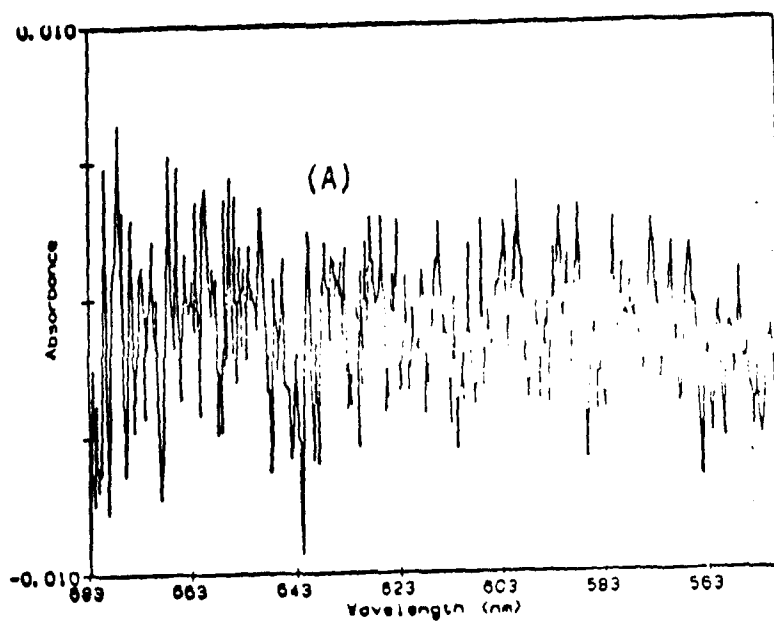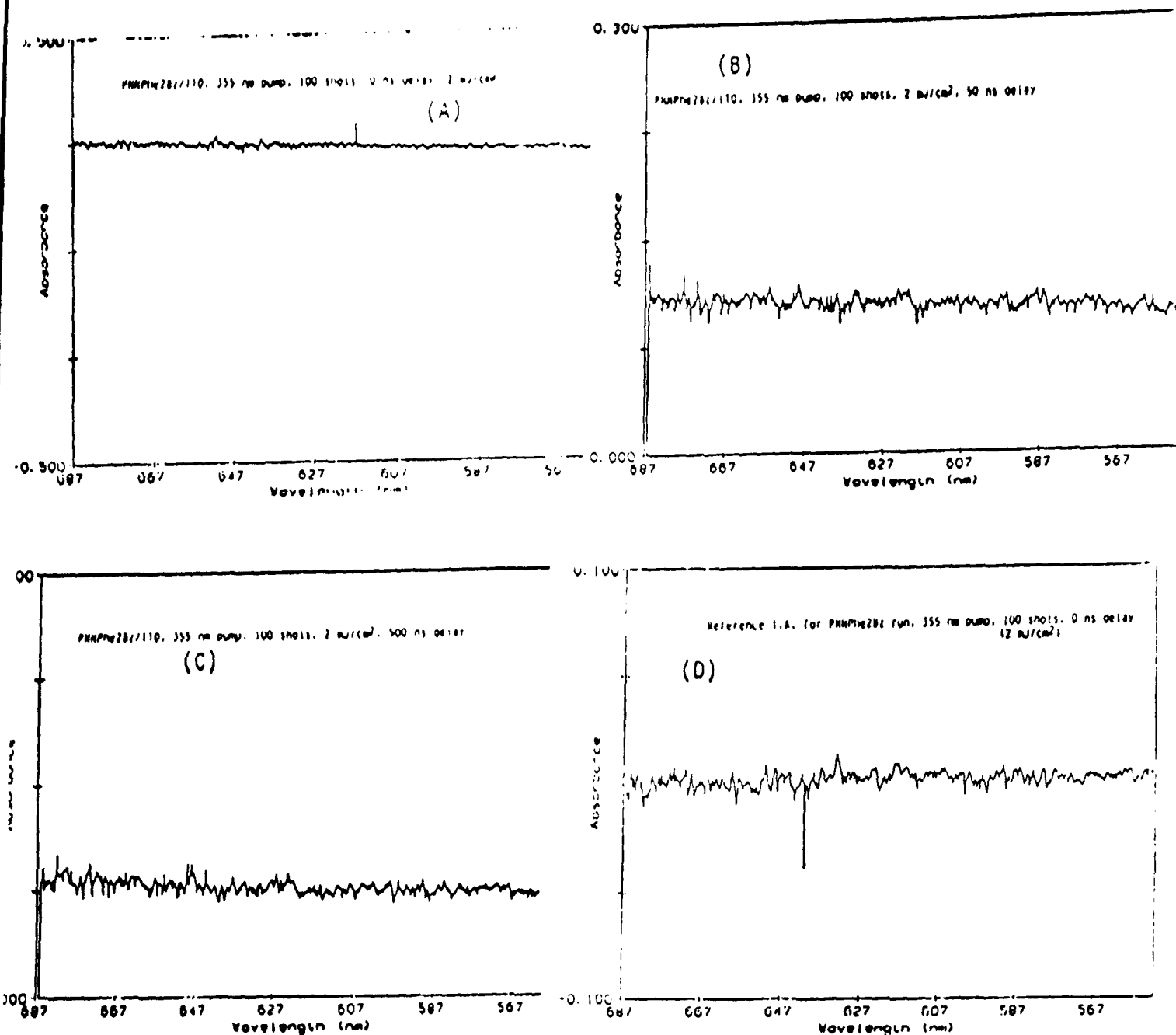
FIGURES 10A-C

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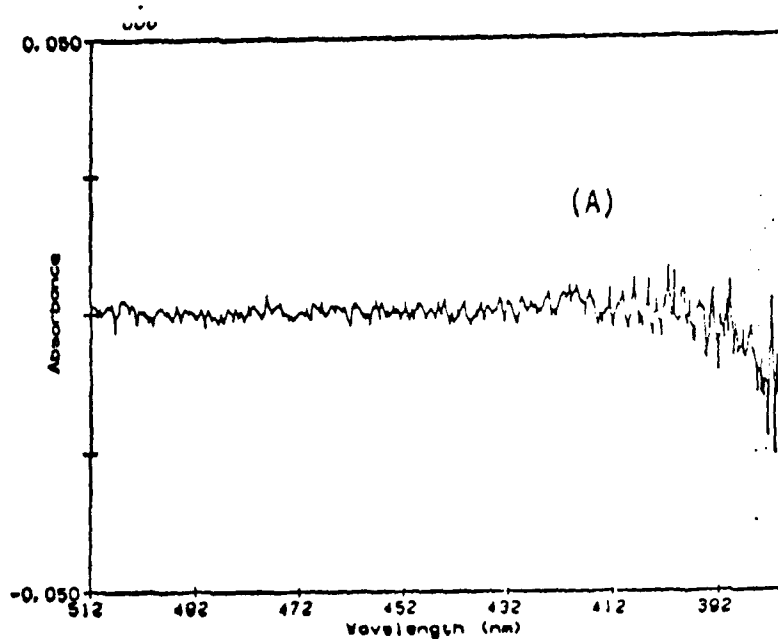
TA Spectra for 4-amino
biphenyl monomer (A) and
PABP (polymer, (B)).
Pump at 532 nm, 8 ns,
2 mJ/cm$^2$, monitored
at 0 ns delay. All
other laser parameters
standard.

FIGURES 11A,B

FIGURES 12: TA spectra for diphenyl amine monomer (A) and polymer (PDPA), 532 nm pump, 8 ns, 2 mJ/cm² pulse, monitored at 0 ns delay, all other laser parameters standard.

**FIGURES 13A-D:**   Laser-induced transient absorption spectra for the PNNPhe2Bz/ITO
SC/CP interface, for a nominal 0 ns delay monitoring time (A),
and for 50 ns (B), 500 ns (C) delays. Note the highly broad-band
nature of the transient absorption of this polymer in this, 560 -
700 nm spectral range, a characteristic of this polymer.
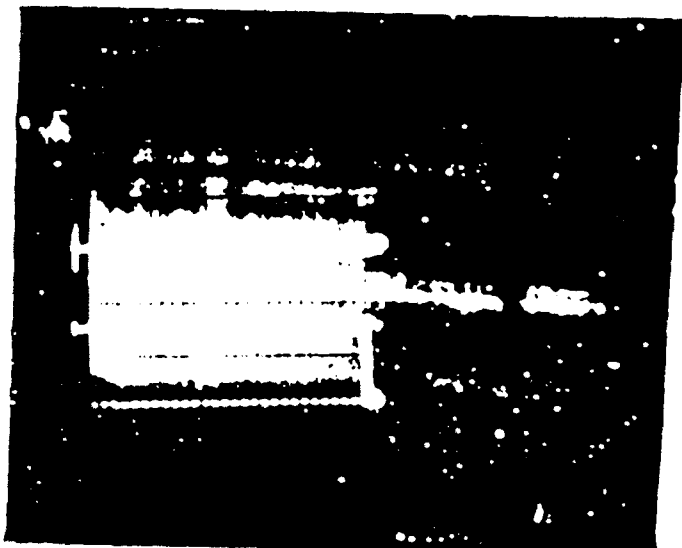
A) X-scale 100 usec/divn.
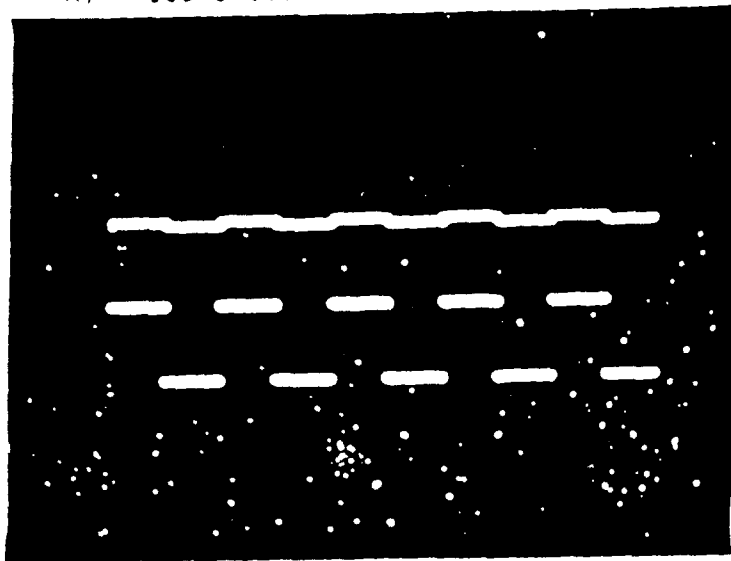


FIGURES 14A-C

A/O Modulated CW laser switching results for the SC/CP interface
CdSe / p(N,N'-Di-Phe-Benzidine). 0.1 msec (100 usec) pulses to
A/O/M driver. Laser energy ca. 8.3 uJ/cm²

__Bottom Trace__: A/O/M driver input (0 to +3 V, 0.1 msec), Y-Scale: 2 V/divn.

__Top Trace__: Output from Si-avalanche photodetector, Y-scale: 5 mV/divn.

B) Falltime: X-scale 1 usec/divn.



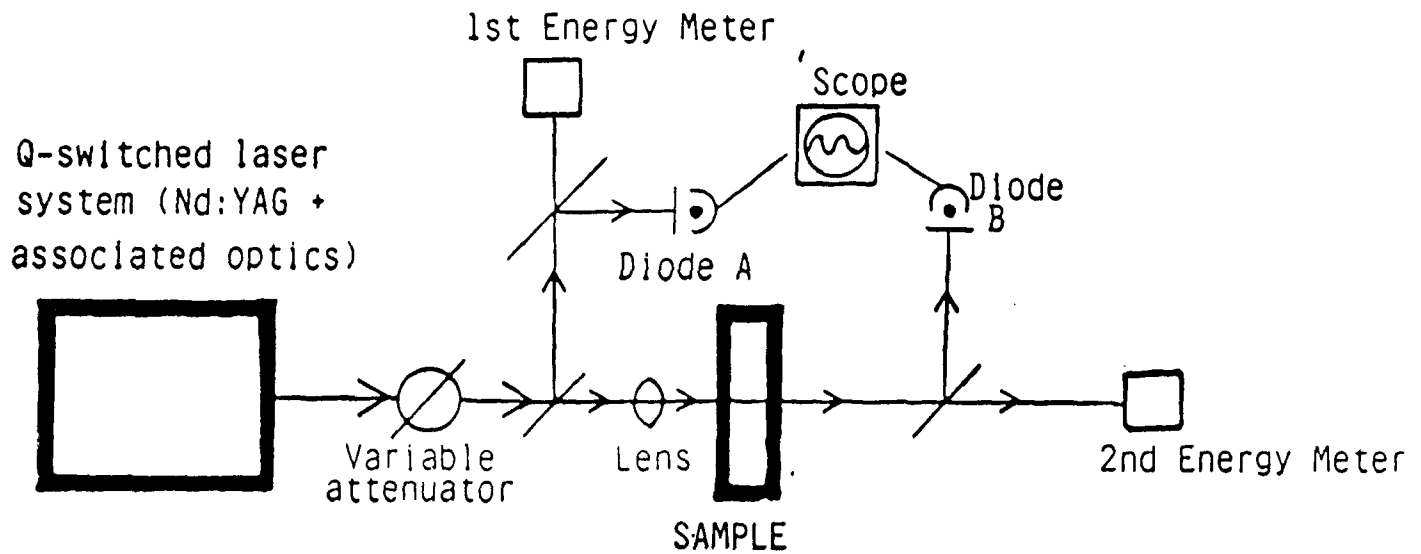C) Risetime: X-scale 100 ns/divn.

FIGURE 15: **Schematic of apparatus for NLO effects** measurement based on nonlinear transmission (NLT) and related techniques.
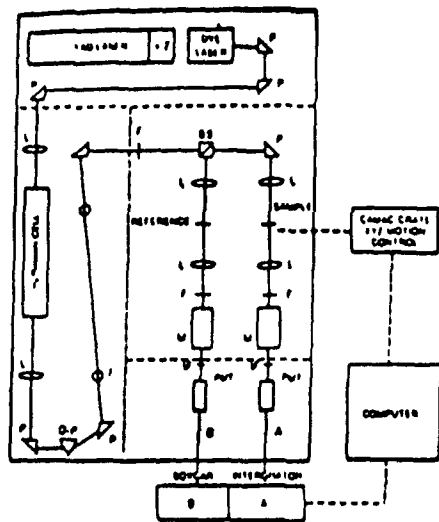


FIGURE 16: Schematic of apparatus for THG measurements with both reference and sample cells, after Khanarian et al.
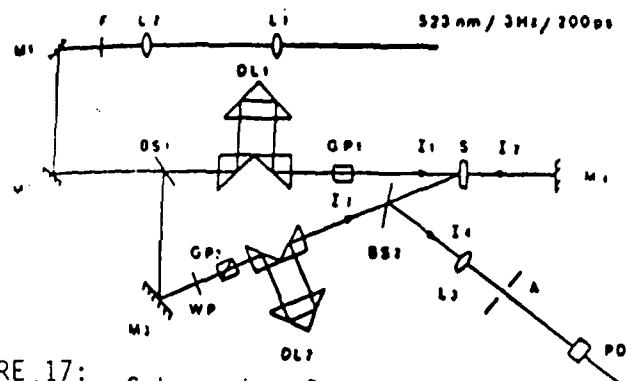
FIGURE 17: Schematic of apparatus for Degenerate Four Wave Mixing (DFWM), after Dennis et al.